



Ganley, W. J., & Van Duijneveldt, J. S. (2015). Controlling Clusters of Colloidal Platelets: The Effects of Edge and Face Surface Chemistries on the Behaviour of Montmorillonite Suspensions. *Langmuir*, 31(15), 4377-4385. <https://doi.org/10.1021/acs.langmuir.5b00047>

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Supporting information for:

Controlling Clusters of Colloidal Platelets: The Effects of Edge and Face Surface Chemistries on the Behaviour of Montmorillonite Suspensions

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Oscillatory Rheology of Montmorillonite Suspensions

Figures S1 to S3 show oscillatory frequency sweeps of montmorillonite suspensions at a range of ionic strengths and weight fractions. These were used to construct rheological phase diagrams in the main report.

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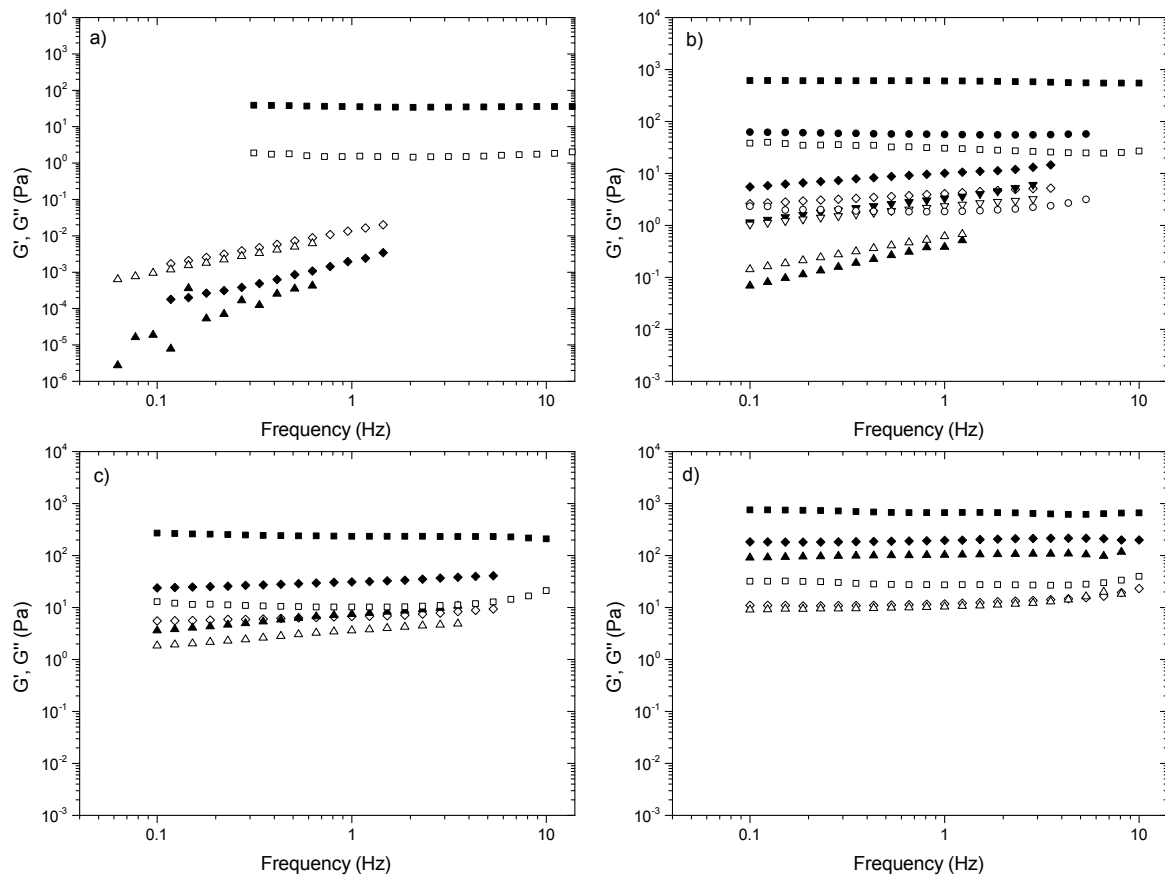


Figure S1: Rheological frequency sweeps for montmorillonite suspensions at (a) 2% wt., (b) 3% wt., (c) 4% wt. and (d) 5% wt. with Na^+ concentrations of 10^{-5} M (diamonds), 10^{-4} M (down triangles), 10^{-3} M (up triangles), 10^{-2} M (circles) and 10^{-1} M (squares). Closed symbols denote elastic moduli G' and open symbols denote viscous moduli G''

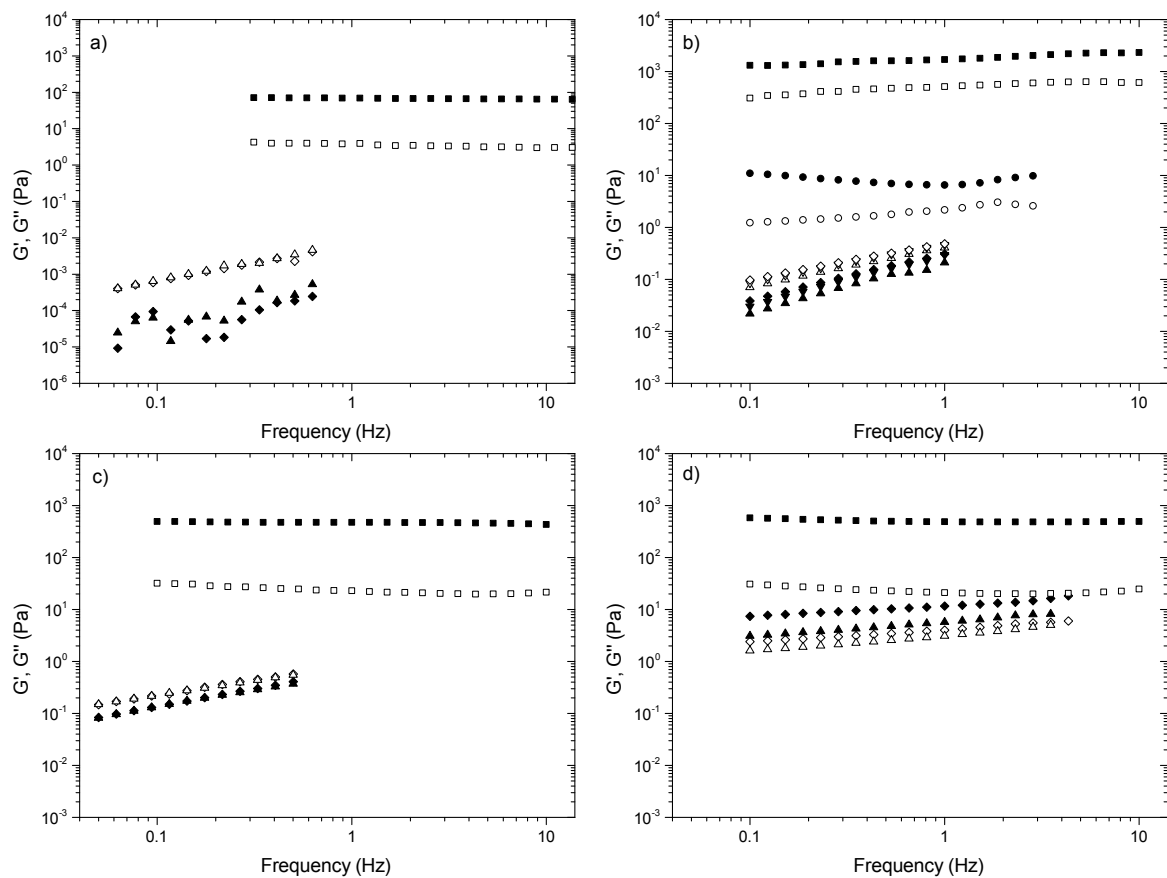


Figure S2: Rheological frequency sweeps for montmorillonite suspensions with $340 \mu\text{mol g}^{-1}$ M1000. Symbols as in figure S1

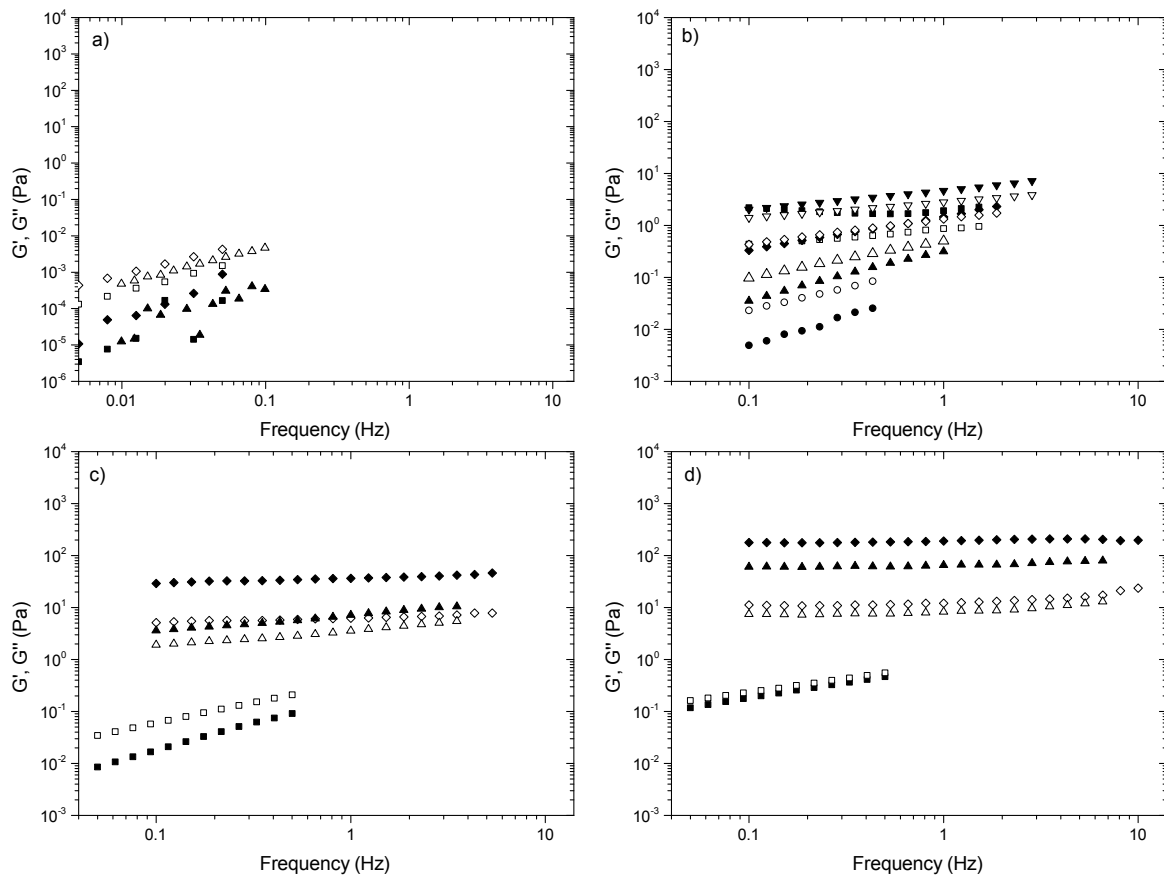


Figure S3: Rheological frequency sweeps for montmorillonite suspensions with $\text{Na}_4\text{P}_2\text{O}_7$ in place of NaCl . Symbols as in figure S1

Small Angle Light Scattering

Figure S4 shows small angle light scattering (SALS) data from 0.25% wt. montmorillonite suspensions at Na^+ concentrations of 10^{-5} M, 10^{-3} M and 10^{-2} M. Table S1 shows the results of fits to the Fisher-Burford model for all SALS curves and table S2 shows the % transmissions for each sample compared to water.

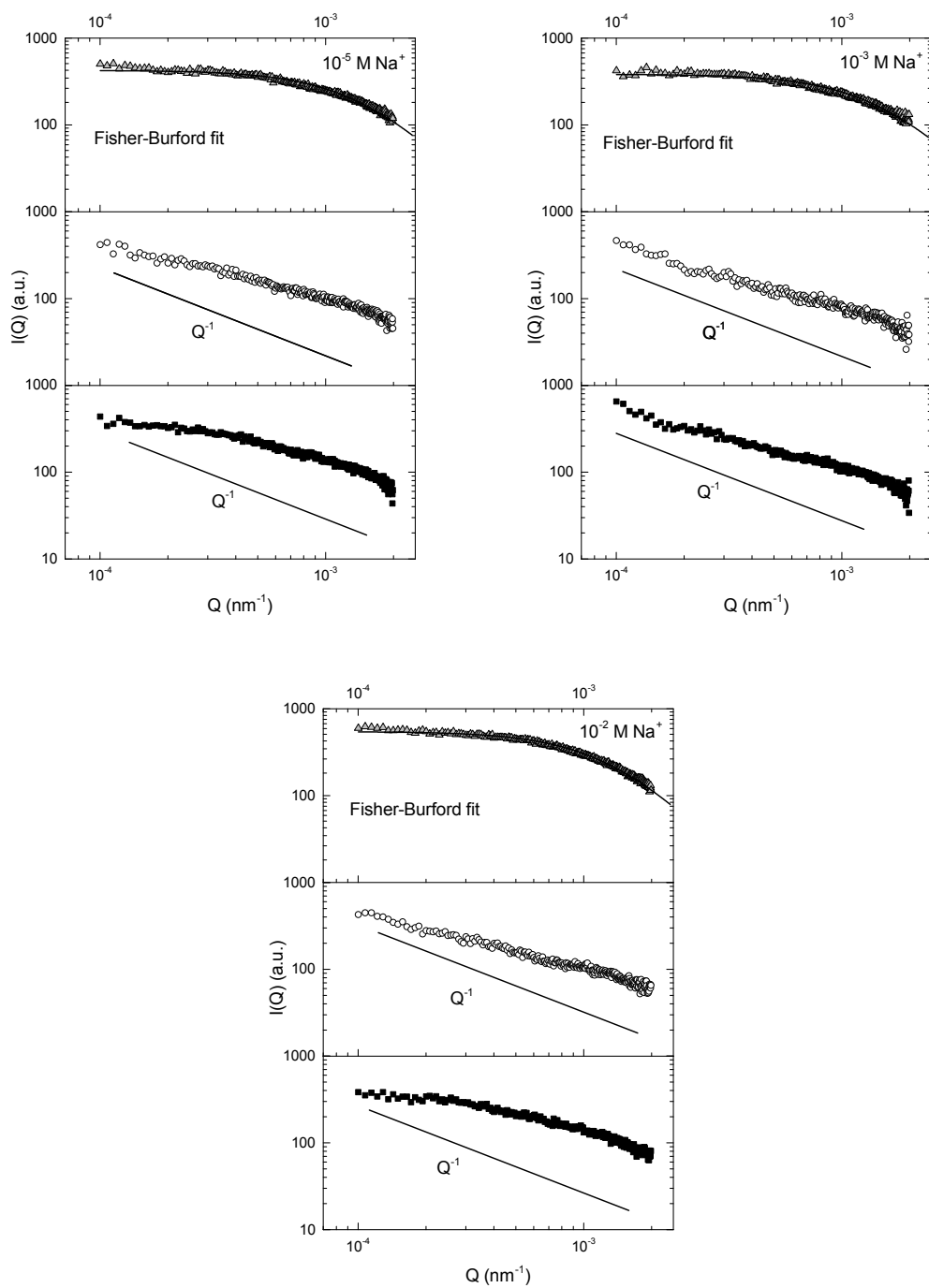


Figure S4: SALS of 0.25% wt. montmorillonite suspensions with 10^{-5} M added Na^+ (upper left), 10^{-3} M added Na^+ (upper right) and 10^{-2} M added Na^+ (lower). Untreated montmorillonite (black squares), with $340 \mu\text{mol g}^{-1}$ M1000 (grey triangles) and with $\text{Na}_4\text{P}_2\text{O}_7$ (open circles). Solid lines on M1000 datasets are fits to the Fisher-Burford model.

Table S1: Results of Fisher-Burford fits to SALS of all measured systems. Numbers correspond to R_g values from Fisher-Burford fits, hyphens to Q^{-1} power law forms and asterisks to scattering that deviates from the Q^{-1} power law but does not fit the Fisher-Burford form

C_{Na^+} (M)	Untreated	M1000	Pyrophosphate
10^{-5}	*	478 ± 4	-
10^{-4}	-	482 ± 2	-
10^{-3}	-	473 ± 4	-
10^{-2}	*	526 ± 3	-
10^{-1}	552 ± 3	*	*

Table S2: Percentage light transmitted through samples in small angle light scattering

Surface Chemistry	C_{Na^+} (M)	% Transmission
Untreated	10^{-5}	95.0
	10^{-4}	93.7
	10^{-3}	92.9
	10^{-2}	92.7
	10^{-1}	91.1
M1000 treated	10^{-5}	88.6
	10^{-4}	88.1
	10^{-3}	88.0
	10^{-2}	87.4
	10^{-1}	81.9
Pyrophosphate treated	10^{-5}	93.8
	10^{-4}	94.6
	10^{-3}	93.9
	10^{-2}	92.9
	10^{-1}	92.2

Suspension Birefringence

A selection of the samples used in rheological measurements were observed through crossed polarisers to detect the alignment of platelets.

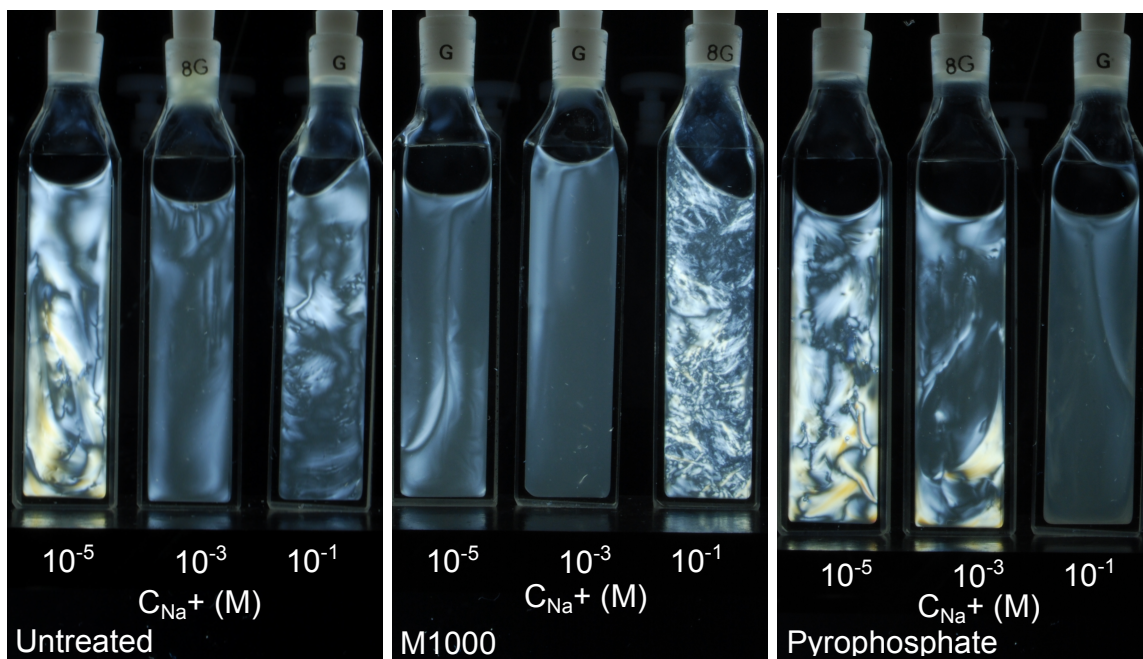


Figure S5: 4 % wt. montmorillonite suspensions from rheological experiments viewed between crossed polarisers

Figure S5 shows birefringence in all samples after the samples are inverted with all three surface treatments across the full range of C_{Na^+} . The presence of birefringence in all samples is consistent with the existence of platelets that have not undergone extensive aggregation.

Wall Slip Analysis

The rheological measurements detailed in this report were carried out using two different upper geometries: a $4^\circ/40$ mm cone and a 20 mm plate. Before using the two geometries the extent of wall slip was examined. This was done by comparing frequency sweeps of a 3% wt. montmorillonite suspension in 10^{-3} M NaCl using the cone and plate at a gap width of $150\ \mu\text{m}$ and the parallel plates at gap widths ranging from 0.5 - 3 mm. Apart from the

geometry used the procedure was identical to that detailed in the main report.

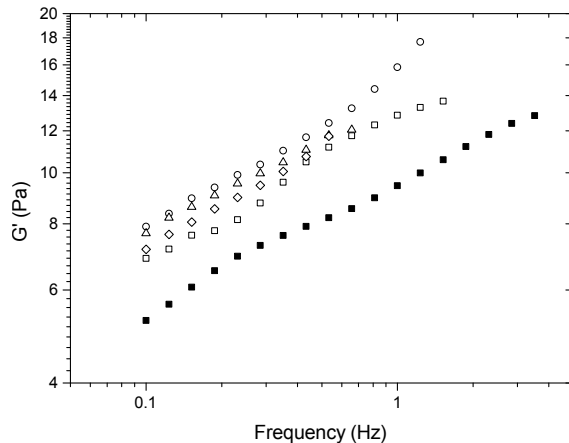


Figure S6: Rheological frequency sweeps for 3% wt. montmorillonite suspensions in 10^{-3} M NaCl using: cone and plate at a gap width of 0.15 mm (closed squares), parallel plates at gap widths of 0.50 mm (open squares), 1.00 mm (open circles), 2.00 mm (open triangles) and 3.00 mm (open diamonds)

Figure S6 shows that use of the parallel plates showed no systematic increase in modulus as gap width increased, suggesting minimal wall slip, whereas the use of the larger diameter cone and plate geometry showed a slightly lower modulus, suggestive of greater slip. The cone and plate geometry did, however allow measurements at higher frequencies due to a lower inertial component associated with the upper cone than the upper plate.

Quantitative measurements of plateau elastic moduli were therefore carried out using the parallel plate geometry at a gap width of 1 mm where slip was minimal, and hence measured moduli were more accurate, whereas for qualitative measurements, those used to define the rheological state of the systems (figures S1 to S3), were carried out using the cone and plate geometry as for those measurements a higher range of frequencies was desirable.